

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09D 11/00	A1	(11) International Publication Number: WO 96/23844 (43) International Publication Date: 8 August 1996 (08.08.96)
(21) International Application Number: PCT/GB96/00076		(81) Designated States: AU, CA, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 16 January 1996 (16.01.96)		
(30) Priority Data: 08/383,105 3 February 1995 (03.02.95) US		Published <i>With international search report.</i>
(71) Applicant: THE GENERAL ELECTRIC COMPANY PLC [GB/GB]; 1 Stanhope Gate, London W1A 1EH (GB).		
(72) Inventor: DENG, Godwin; 1460 Fairlane Drive, 107 Schaumburg, IL 60193-3530 (US).		
(74) Agent: McGOWAN, Nigel, George; GEC Patent Dept., Waterhouse Lane, Chelmsford, Essex CM1 2QX (GB).		

BEST AVAILABLE COPY

(54) Title: AN INK COMPOSITION

(57) Abstract

This invention relates to a jet ink composition and a method for printing on wet glass, PET, and aluminum surfaces under humid conditions messages having good penetration, adhesion and abrasion resistance. The ink composition comprises an organic solvent, a flexible thermoplastic urethane resin, silicone resin, a silane, and a colorant.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

An Ink Composition

The present invention relates to ink printing compositions, particularly for printing on glass, polyethylene terephthalate (PET), and aluminum substrates and, more particularly, for printing on containers made of 5 glass, PET, aluminum, or other substrates that may be subjected to humid conditions whereby moisture is created on the outside of such containers, and to related methods of printing.

Ink jet printing is a well-known technique by which 10 printing is accomplished without contact between the printing device and the substrate on which the printed characters are deposited. Briefly described, ink jet printing involves the technique of projecting a stream of ink droplets to a surface and controlling the direction of 15 the stream electronically so that the droplets are caused to form the desired printed image on that surface. This technique of noncontact printing is particularly well-suited for application of characters onto irregularly shaped surfaces, including, for example, the bottom of 20 glass or metal beverage containers.

Reviews of various aspects of ink jet printing can be found in publications: Kuhn et al., *Scientific American*, April, 1979, 162-178; and Keeling, *Phys. Technol.*, 12(5), 196-303 (1981). Various ink jet apparatuses are described 25 in the following U.S. patents: 3,060,429, 3,298,030, 3,373,437, 3,416,153, and 3,673,601.

In general, an ink jet composition must meet certain rigid requirements to be useful in ink jet printing operations. These relate to viscosity, resistivity, solubility, compatibility of components and wettability of 5 the substrate. Further, the ink must be quick-drying and smear resistant, must be capable of passing through the ink jet nozzle without clogging, and must permit rapid cleanup of the machine components with minimum effort.

Many of the surfaces on which ink jet printing is 10 utilized are nonporous, such as the above-mentioned beverage container. The ink used for these applications must adhere well to the nonporous substrate and normally must be water-resistant.

Many beverage manufacturers fill the containers with 15 chilled beverages, frequently under humid conditions. The moisture that condenses on the container surfaces poses a severe problem in obtaining penetration, good adhesion of the ink, abrasion and smear resistance of the printed codes.

20 Several ink compositions known heretofore are not suitable for the above use. For example, UK Patent Application GB 2,105,735 discloses a jet ink composition comprising an oil soluble dye-impregnated polyurethane latex dispersed in an aqueous medium.

25 U.S. Patent 4,680,332 discloses a jet ink composition comprising a water insoluble polymer such as a polyacrylate dispersed in a liquid medium, the polymer containing therein an oil soluble dye, and a nonionic

stabilizer permanently attached thereto.

U.S. Patent 5,207,825 discloses a jet ink composition which comprises an aqueous liquid vehicle, a colorant, and a polymeric additive which is a substituted bisphenol A derivative.

U.S. Patent 5,080,716 discloses a jet ink composition comprising a recording agent, a liquid medium capable of dissolving or dispersing the recording agent, and a substituted benzene or toluene sulfonamide compound.

U.S. Patent 5,254,158 discloses an ink composition which comprises an aqueous liquid vehicle, a colorant, and an additive selected from the group consisting of amine alkoxylates, sorbitan monoester alkoxylates, alkylene oxide adducts of glycerin, and mixtures thereof.

U.S. Patents 5,215,577 and 5,178,671 disclose jet ink compositions comprising a recording agent and a liquid medium for dissolution or dispersion thereof, the recording agent being an aromatic sulfonated diazo compound.

U.S. Patent 5,131,949 discloses a jet ink composition including a recording agent, a liquid medium capable of dissolving or dispersing the recording agent, and a compound having an amide group.

U.S. Patent 5,213,613 discloses a jet ink comprising a recording agent and a liquid medium capable of dissolving or dispersing the recording agent therein, wherein the ink contains an imide compound and at least one compound selected from the group consisting of urea,

thiourea and derivatives thereof, and volatile alkaline compounds.

U.S. Patent 4,692,188 discloses a process for the preparation of jet ink compositions, comprising (1) dissolving in a water-immiscible organic solvent a polymer composition and an organic oil soluble dye; (2) adding an aqueous phase water surfactant mixture thereto; (3) affecting emulsification thereof; and (4) subsequently evaporating from the aforementioned mixture the solvent thereby resulting in an ink with the dye trapped in the polymer particles suspended in the aqueous phase. The polymer compositions include polycarbonates, polystyrene, polymethacrylates and copolymers thereof.

U.S. Patent 5,393,331 discloses an ink composition for use in drop-on-demand ink jet operations for printing on porous substrates such as paper and card board, which has low levels of volatile organic compounds and that is both non-teratogenic and non-carcinogenic.

All of the water based jet ink compositions disclosed by the above references are generally directed to ink compositions suitable for printing on paper and are not considered suitable for printing on cold glass, PET, and aluminum surface, especially under humid conditions conducive for the moisture to condense on the surface.

Other attempts to produce ink compositions that will provide penetration, good adhesion and abrasion resistance to messages printed on wet glass, PET and aluminum surfaces have been unsuccessful. Poor adhesion and poor

print quality were common, especially when the cold-fill process was in a highly humid environment. Therefore, a need exists for a jet ink composition which can be used to print messages on wet glass, PET, and aluminum surfaces 5 and able to penetrate moisture without smudging, smearing or rubbing off.

A need also exists for an ink composition for use in ink jet applications that can be printed onto cold, wet glass, PET and aluminum container surfaces under humid 10 conditions.

The present invention provides ink compositions capable of being printed onto cold, wet glass, PET, and aluminum surfaces under humid conditions and providing good contrast. The ink compositions embodying the 15 invention are capable of penetrating condensation on a glass, PET, and aluminum surfaces, such as the thin layer of condensation often found during the production of beverages in glass, PET, and aluminum containers under refrigerated conditions.

20 The ink composition of the present invention comprises an organic solvent, a colorant, polyurethane binder, a silicone resin, and silane. An additional resin and/or a surfactant may also be used in the composition.

The present invention also provides a method of 25 forming printed images on cold wet glass, PET, and aluminum surfaces using the ink composition of the present invention. In accordance with the invention the method comprises projecting a stream of droplets of said ink

composition onto said surface and controlling the direction of said stream electronically so that said droplets form the desired printed image on said surface.

In general, the ink compositions of the present invention exhibit the following characteristics for use in ink jet printing systems: (1) a viscosity from about 1.6 to about 7.0 centipoises at 25° C; (2) an electrical resistivity from about 50 to about 2000 ohm-cm; and (3) a sonic velocity from about 1200 to about 1300 meters/second.

SOLVENTS

Organic solvents suitable for the ink composition of the instant invention include ketones such as acetone, methyl ethyl ketone, diethyl ketone, cyclohexanone, and the like; esters such ethyl acetate, propyl acetate, butyl acetate, amylacetate, and the like; alcohols such methanol, ethanol, n-propanol, isopropanol, n-butanol, i-butanol, t-butanol, n-pentanol, n-hexanol, and the like; glycols such as ethylene glycol, propylene glycol, glycerin, diethylene glycol, and the like, glycol ethers such as ethylene glycol dimethyl ether, ethylene glycol diethylether, cellosolve, diethylene glycol dimethylether, diethylene glycol diethylether, and the like, and other solvents commonly known to one of ordinary skilled in the art, as well as mixtures of two or more of the foregoing. Methyl ethyl ketone is a preferred solvent, optionally in admixture with another solvent, preferably ethanol.

POLYURETHANES

Flexible thermoplastic polyurethane resins are used as binders in the preparation of the ink compositions of the instant invention. Flexible thermoplastic urethanes are produced by the reaction of diols and diisocyanates. Examples of diols include ethylene glycol, propylene glycol, propanediol, butanediol, polyethylene glycol, polypropylene glycol, polyethylene glycol adipate diol, polyethylene glycol succinate diol, polytetrahydrofuran diol, and the like. Examples of diisocyanates include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate, and the like. Polyurethanes made from polypropylene glycol and 4,4'-diphenylmethane diisocyanate are preferred.

Polyurethanes having weight average molecular weight in the range of about 4,000 to about 12,000 are preferred and polyurethanes having weight average molecular weight in the range of about 7,000 to about 9,000 are even more preferred.

Examples of preferred urethane polymers that are useful in the present invention include, but are not limited to, the flexible thermoplastic polyurethane solutions sold under the commercial name of Surkopak by Kane International Corp., Rye, New York. A variety of grades of polyurethanes are sold under this name and include Surkopak 2135, Surkopak 5299, Surkopak 5244, Surkopak 5255, Surkopak 2X, Surkopak 5322, Surkopak

5311, and Surkopak XL. They are normally used to modify nitrocellulose based printing inks for flexo and gravure applications on flexible packaging substrates such as polyethylene, polypropylene, polyester, and cellulose. The 5 physical properties of the polyurethane solutions are presented in Table 1 below.

Table 1. Properties of the Surkopak Polyurethane Resins

Grade	2135	5299	5244*	5255	2X	5322**	5311	XL
Solids %	80-85	80-85	73-78	73-78	65-70	68-73	63-68	68-73
Visco-sity	15-25	25-30	12-16	25-30	40-50	6-8	30-40	15-20
Solvent	A	A	E	E	E	E/A	E	E/A
Flash Point, °C	12	12	-4	-4	-4	-4	-4	-4

A = Alcohol; E = Ester; E/A = Mixture of E and A

* Weight Average Molecular Weight Range 18,000 - 22,000

** Weight Average Molecular Weight Range 7,000 - 9,000

These polyurethanes are non-reactive and are essentially free of isocyanate groups. Among these preferred polyurethane solutions, even more preferred is Surkopak 5322, which is a polyurethane composed of 5 polypropylene glycol and 4,4'-diphenylmethane diisocyanate. Surkopak 5322 is sold as a solution in a mixed solvent containing ethyl acetate and isopropanol.

The concentration of solid polyurethane resin in the ink composition is in the range of about 1 percent to 10 about 20 percent by weight, preferably in the range of about 3 percent to about 15 percent by weight, and more preferably in the range of about 5 percent to about 10 percent by weight. If the polyurethane is commercially sold as a solution, as in the case of Surkopak, the amount 15 of the polyurethane solution to be used to prepare the ink is calculated from the concentration of the polyurethane in the solution. Thus, in EXAMPLE 1 below, 11 g of the Surkopak 5322 (conc. 68-73%) were used to obtain an ink having about 7.7 g of polyurethane.

20

COLORANTS

The ink composition comprises a colorant which is a dye that imparts the desired color to the printed message. Any dye that may be dissolved in the ink composition may 25 be used in the instant invention. For instance, U.S. Patent 5,254,158, and UK Patent Application GB 2,105,735 list several examples of dyes. All of these dyes and pigments may be used in the instant invention. Examples

of dyes applicable to the present invention include, but are not limited to, the yellow dyes such as C.I. Solvent Yellow 19 (C.I. 13900A), C.I. Solvent Yellow 21 (C.I. 18690), C.I. Solvent Yellow 61, C.I. Solvent Yellow 80, 5 FD&C Yellow #5, Yellow Shade 16948, Acid Yellow 23, Levaderm Lemon Yellow (Mobay), Spirit Fast Yellow 3G, Aizen Spilon Yellow C-GNH (Hodagaya Chemical Co.), Pergasol Yellow CGP (Ciba-Geigy), and the like, the orange dyes such as C.I. Solvent Orange 1 (C.I. 11920), C.I. 10 Orange 37, C.I. Orange 40, Diaresin Orange K (Mitsubishi Chemical Industries, Ltd.), Diaresin Orange G (Mitsubishi Chemical Industries, Ltd.), Sumiplast Orange 3G (Sumitomo Chemical Co., Ltd.), and the like, red dyes such as C.I. Solvent Red 8, C.I. Solvent Red 81, C.I. Solvent Red 82, 15 C.I. Solvent Red 84, C.I. Solvent Red 100, Cibacron Brilliant Red 38-A (Aldrich Chemical Co.), Drimarene Brilliant Red E-6A (Pylam, Inc.), Acid Red 92, Reactive red 31 (ICI America), and the like, pink dyes such as Diaresin Pink M (Mitsubishi Chemical Industries, Ltd.), 20 Sumiplast Pink RFF (Sumitomo Chemical Co.), Direct Brill Pink B Ground Crude (Crompton & Knowles), and the like, violet dyes such as C.I. Solvent Violet 8, C.I. Solvent Violet 21, Diaresin Violet (Mitsubishi), Diaresin Violet D, Sumiplast Violet RR (Sumitomo), and the like, blue dyes 25 such as C.I. Solvent Blue 2, C.I. Solvent Blue 11, C.I. Solvent Blue 25, C.I. Solvent Blue 36, C.I. Solvent Blue 55, and the like, green dyes such as C.I. Solvent Green 3 and the like, brown dyes such as C.I. Solvent Brown 3 and

Diaresin Brown A (Mitsubishi), and the like, black dyes such as C.I. Solvent Black 3, C.I. Solvent Black 5, C.I. Solvent Black 7, C.I. Solvent Black 22, C.I. Solvent Black 27, C.I. Solvent Black 29, Acid Black 123, and the like.

5 The colorant is present in the ink composition in an amount required to produce the desired contrast and readability. The colorant is preferably present in the range of about 2 percent to about 12 percent by weight, more preferably in the range of about 4 percent to about
10 10 percent by weight, and even more preferably in the range of about 5 percent to about 7 percent by weight.

SURFACTANTS

The jet ink composition may preferably contain a
15 surfactant, which may be anionic, cationic, nonionic, or amphoteric. Examples of anionic surfactants are, but are not limited to, alkylbenzene sulfonates such as dodecylbenzene sulfonate, alkynaphthyl sulfonates such as butyl or nonyl naphthyl sulfonate, dialkyl sulfosuccinates
20 such as diamyl sulfosuccinate, alcohol sulfates such as sodium lauryl sulfate, and perfluorinated carboxylic acids such as perfluorodecanoic acid and perfluorododecanoic acid. Nonionic surfactants include the alkylesters of polyethylene glycol, fatty acid esters of glycerol, fatty
25 acid esters of glycol, and the like, and fluoroochemical surfactants such as FC 430, FC 431, FC 740, FC 120, FC 248, FC 352, FC 396, FC 807, and FC 824, which are available from 3M Co. Cationic surfactants include

alkylamines, amine oxides, amine ethoxylates, alkyl hydroxyalkyl imidazolines, quaternary ammonium salts, and amphoteric surfactants include the alkylbetaines, the amidopropylbetaines, and the like. The surfactant FC 430, 5 which is a mixture of fluoroaliphatic polymeric acrylate esters, is a preferred surfactant.

The solid surfactant made into solution may be present in the jet ink composition in the range of about 0.007 percent to about 0.05 percent by weight, preferably 10 in the range of about 0.005 percent to about 0.04 percent by weight, and more preferably in the range of about 0.01 percent to about 0.03 percent by weight.

SILICONE ADDITIVES

15 The jet ink composition may preferably contain a silicone resin. Examples of silicone resins include, but are not limited to, dimethyl silicone resin, methylphenyl silicone resin, and methyltrifluoropropyl silicone resin. Silicone resins are commercially available from Dow 20 Corning Corp. and GE Silicones. A preferred silicone resin is the silicone resin DC6-2230 (Dow Corning), which is a polysiloxane having methyl (48%), phenyl (44%), hydroxyl (4%), O-butyl (2%), and O-propyl(1%) substituents.

25 The silicone resin may be present in the jet ink composition in the range of about 0.5 percent to about 10 percent by weight, preferably in the range of about 1 percent to about 6 percent by weight, and more preferably

in the range of about 2 percent to about 4 percent by weight.

SILANES

5 The jet ink composition may preferably contain a silane coupling agent. Examples of silanes that may be useful are, but are not limited to, epoxyalkyl alkoxysilanes, aminoalkyl alkoxysilanes such as (4-aminopropyl)triethoxysilane and [γ -(β -aminoethylamino)-propyl]trimethoxysilane, vinyltris(β -methoxyethoxy)silane, (γ -methacryloxypropyl)-trimethoxysilane, vinylbenzyl cationic silane, (γ -chloropropyl)trimethoxy-silane, and the like. Additional examples of silanes can be found, e.g., in Kirk-Othmer - Encyclopedia of Chemical Technology, 3rd edition (John-Wiley & Sons). One preferred silane is the A187 silane from Union Carbide Corp., which is glycidoxypropyl trimethoxysilane.

15 The silane may be present in the jet ink composition in the range of about 0.1 percent to about 5 percent by weight, preferably in the range of about 0.3 percent to about 4 percent by weight, and more preferably in the range of about 0.5 percent to about 2.5 percent by weight.

OTHER RESINS

25 The jet ink composition may also preferably contain an additional resin. Other resins may be added to the ink to add hardness and improve abrasion and smear resistance. Other resins may include rosin resins. Examples of rosin

resins are Pentalyn H synthetic resin, a pentaerythritol ester of a rosin that has been stabilized by hydrogenation. Also, Foral 85 resin, a thermoplastic glycerol ester of a hydrogenated resin. Both are sold by 5 Hercules, Inc. These resins may also include various acrylic resins such as polyalkylacrylates, the polyalkylmethacrylates, and copolymers thereof. Additional examples of acrylic resins are polymethacrylate, polyethylacrylate, 10 polyethylmethacrylate, polybutylmethacrylate, polymethylmethacrylate, polyhydroxyethylmethacrylate, copolymers of the acrylates, and the like. Several acrylic resins are commercially available from Rohm & Haas Co. A copolymer containing ethylmethacrylate is sold 15 under the name of Acryloid B-72. A polymer of isobutylmethacrylate is sold under the name of Acryloid B-67. A copolymer of methylmethacrylate and ethylacrylate is sold under the name of Acryloid B-44. One preferred acrylic resin is Acryloid B-66, which is a copolymer of 20 methylmethacrylate and butylmethacrylate.

The additional resin may be present in the jet ink composition in the range of about 1 percent to about 12 percent by weight, preferably in the range of about 2 percent to about 10 percent by weight, and more preferably 25 in the range of about 3 percent to about 8 percent by weight.

OTHER ADDITIVES

The jet ink composition may contain in addition additives for adjusting the viscosity, electrical resistivity, and the speed of evaporation. The preferred 5 range of viscosity is about 1.5 centipoise to about 6.0 centipoise. The preferred resistivity is about 500 ohm-cm to about 1500 ohm-cm.

The compositions of the present invention may contain conductivity agents. If present, they usually are present 10 in amounts of from about 0.0 percent to about 2.0 percent. Examples of suitable conductivity agents include dimethylamine hydrochloride, diethylamine hydrochloride, lithium nitrate, and hydroxylamine hydrochloride. Sufficient conductivity is offered by the dye, solvent 15 black 29, in the presence of the ethanol used in the ink. Humectants may be used in the formulations. Humectants include glycerin, ethylene glycol, and the like. Various, known viscosity modifying agents may be added, as needed, to adjust the viscosity of any given ink 20 formulation.

The jet ink formulation may be prepared by any known methods. In one method, all the desired ingredients are combined in a mixer or a mixing vessel and mixed sequentially until a homogeneous solution is obtained.

25 The jet ink composition may be generally jet printed on to the surface of a wet glass, PET, and aluminum article such as a glass bottle, PET bottle, or aluminum can. Specifically, the jet ink is used to print messages

on glass, PET, and aluminum bottles and cans that are used to fill cold beverages including soft drinks such as Pepsi Cola®, Coca Cola®, RC Cola®, 7-UP®, Sprite®, and the like, beer, wine, wine coolers, liquors, and the like.

5 pharmaceuticals, and cosmetics. The jet ink of the instant invention may be jet applied on to a variety of glasses, including soda-lime glasses, borosilicate glasses, alumino-silicate glasses, lead glasses, borate glasses, and the like. The above specified types of glass

10 may contain a coating.

All percentages expressed herein are percentages by weight, based on the total weight of the ink composition of the present invention, unless otherwise indicated.

15 The following example further illustrates the present invention but, of course, should not be construed as in any way limiting its scope.

EXAMPLE 1

20 A jet ink composition was prepared by employing the following formulation:

	<u>Ingredient</u>	<u>Percent by weight</u>
	Methyl ethyl ketone	71.3
	Silicone DC6-2230 (Dow Corning)	3.0
25	Acryloid B-66 (Rohm & Haas)	5.0
	Surkopak Polyurethane 5322	11.0
	Solvent Black 29 Dye (Ciba-Geigy)	6.0
	Ethanol CDA-19 200 Proof (EMCO Chemical)	2.0

Silane A187 (Union Carbide)	1.5
FC 430 10% in MEK (3M Co.)	0.2
	100.0

5

The above ink formulation was prepared and tested on
a wide range of glass, PET, and aluminum bottles
simulating cold-fill humid conditions. Printer
runnability testing was also carried out. The jet ink
10 performed satisfactorily.

Images can be printed on a glass, PET, and aluminum
surface under humid conditions using the jet ink
composition of the instant invention by projecting a
stream of droplets of the ink to the surface and
15 controlling the direction of the stream electronically so
that the droplets form the desired printed image on the
surface.

CLAIMS:

1. An ink composition for printing on glass, PET, and aluminum surfaces under humid conditions messages having good adhesion and abrasion resistance, said 5 composition comprising an organic solvent, a flexible thermoplastic polyurethane resin, a colorant, a silicone resin, and a silane.
2. An ink composition as claimed in claim 1, 10 wherein said composition has (1) a viscosity from 1.6 to 7.0 centipoises at 25° C; (2) an electrical resistivity from 50 to 2000 ohm-cm; and (3) a sonic velocity from 1200 to 1300 meters/second.
3. An ink composition as claimed in claim 2, 15 wherein said solvent comprises methyl ethyl ketone.
4. An ink composition as claimed in claim 1, 2 or 3, wherein said polyurethane resin comprises polypropylene 20 glycol and 4,4'-diphenylmethane diisocyanate.
5. An ink composition as claimed in claim 1, 2 or 3, wherein said polyurethane resin comprises Surkopal 5322.
- 25 6. An ink composition as claimed in any one of the preceding claims, wherein said polyurethane resin is present in the concentration range of 3 percent to 15

percent by weight.

7. An ink composition as claimed in claim 6,
wherein said polyurethane resin is present in the
5 concentration range of 5 percent to 10 percent by weight.

8. An ink composition as claimed in any one of the
preceding claims, wherein said colorant is Solvent Black
29.

10

9. An ink composition as claimed in any one of the
preceding claims, wherein said colorant is present in the
range of 4 to 10 percent by weight.

15

10. An ink composition as claimed in any one of the
preceding claims, wherein said composition further
comprises an additional resin, to improve hardness,
abrasion resistance, and smear resistance.

20

11. An ink composition as claimed in claim 10,
wherein said additional resin is an acrylic resin.

25

12. An ink composition as claimed in claim 11,
wherein said acrylic resin is a copolymer of
methylmethacrylate and butylmethacrylate and is present in
the range of 2 to 10 percent by weight.

13. An ink composition as claimed in claim 12,

wherein said acrylic resin is present in the range of 4 to 7 percent by weight.

14. An ink composition as claimed in claim 10,
5 wherein said additional resin is a rosin resin.

15. An ink composition as claimed in claim 14,
wherein said rosin resin is a pentaerythritol of a
glycerol ester of a hydrogenated rosin.

10

16. An ink composition as claimed in any one of the preceding claims, wherein said silicone resin is Dow Corning silicone DC6-2230 and is present in the range of 1 to 5 percent by weight.

15

17. An ink composition as claimed in claim 16,
wherein said silicone resin is present in the range of 2 to 4 percent by weight.

20

18. An ink composition as claimed in any one of the preceding claims, wherein said silane is Union Carbide Silane A187 and is present in the range of 0.5 to 2.5 percent by weight.

25

19. An ink composition as claimed in any one of the preceding claims, wherein said composition further comprises a surfactant.

20. An ink composition as claimed in claim 19,
wherein said surfactant is FC 430 from 3M Co. and is
present in the range of 0.01 to 0.2 percent by weight.

5 21. An ink composition as claimed in any one of the
preceding claims, wherein said composition further
comprises ethanol.

10 22. An ink composition as claimed in claim 21,
wherein said ethanol is present in the range of 1 percent
to 5 percent by weight.

15 23. A method of forming images on wet glass, PET;
and aluminum surfaces under humid conditions using an ink
composition as claimed in any one of the preceding claims,
said method comprising projecting a stream of droplets of
said ink composition to said surface and controlling the
direction of said stream electronically so that said
droplets form the desired printed image on said surface.

20

24. An ink composition as claimed in claim 1,
wherein said flexible thermoplastic polyurethane resin is
present in the range of from 5 percent to 10 percent by
weight of said composition, said colorant is present in
25 the range of from 4 percent to 10 percent by weight of
said composition, said silicone resin is present in the
range of from 2 percent to 4 percent by weight of said
composition, and said silane is present in the range of

from 0.5 percent to 2.5 percent by weight of said
composition.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 96/00076

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09D 11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by characteristic symbols)

IPC6: C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electrical data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CLAIMS, JAPIO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category ^a	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A2, 0616017 (CANON KABUSHIKI KAISHA), 21 Sept 1994 (21.09.94). --	1-24
A	US, A, 4337183 (EDGARDO SANTIAGO), 29 June 1982 (29.06.82). --	1-24
A	US, A, 5334690 (MARKUS A. SCHAFHEUTLE ET AL), 2 August 1994 (02.08.94). --	1-24
A	EP, A2, 0290359 (EASTMAN KODAK COMPANY), 9 November 1988 (09.11.88). --	1-24

 Further documents are listed in the continuation of Box C. See patent family annex.

- Special category of cited documents
- "A" document defining the general area of the art which is not considered to be of particular relevance
- "B" other document not published on or after the international filing date
- "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other event
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "Z" document number of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

3 April 1996

02.05.96

Name and mailing address of the ISA/

European Patent Office, P.O. 5818 Patentlan 2
NL-2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Telex 31 651 epo nl
Fax: (+ 31-70) 340-3016

Authorized officer

BARBRO NILSSON

INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 96/00076

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>Dialog Information Services, file 347, JPO & JAPIO, Dialog accession no. 04501680, MITSUBISHI ELECTRIC CORP: "Ink composition", &JP,A, 6145580, November 09, 1992</p> <p>---</p> <p>-----</p>	1-24

INTERNATIONAL SEARCH REPORT
Information on patent family members

05/02/96

International application No.

PCT/GB 96/00076

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0616017	21/09/94	NONE	
US-A- 4337183	29/06/82	NONE	
US-A- 5334690	02/08/94	AU-B- 666020 AU-A- 4180493 BR-A- 9302797 CA-A- 2099086 DE-A- 4222530 EP-A- 0582088 JP-A- 6157698	25/01/96 13/01/94 16/02/94 10/01/94 13/01/94 09/02/94 07/06/94
EP-A2- 0290359	09/11/88	CA-A- 1326313 DE-D, T- 3888229 JP-A- 1045458 US-A- 4847316	18/01/94 08/09/94 17/02/89 11/07/89

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

BLACK BORDERS

IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

FADED TEXT OR DRAWING

BLURRED OR ILLEGIBLE TEXT OR DRAWING

SKEWED/SLANTED IMAGES

COLOR OR BLACK AND WHITE PHOTOGRAPHS

GRAY SCALE DOCUMENTS

LINES OR MARKS ON ORIGINAL DOCUMENT

REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.